Direct Determination of Product Branching for the NH$_2$ + NO Reaction at Temperatures between 302 and 1060 K

Joonbum Park and M. C. Lin*
Department of Chemistry, Emory University, Atlanta, Georgia 30322
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The branching ratio of the two product channels of the NH$_2$ + NO reaction, $\alpha$ and $\beta$ for the formation of N$_2$H + OH and N$_2$ + H$_2$O, respectively, have been determined independently at temperatures between 302 and 1060 K by mass spectrometry. For $\beta$ determination, the concentration of H$_2$O was measured directly, whereas for $\alpha$, the yield of OH was monitored by the CO$_2$ formed by its reaction with added CO. Both [H$_2$O] and [CO$_2$] were carefully calibrated with different standard mixtures before each measurement. $\alpha$ was found to increase gradually from 0.11 ± 0.02 at 302 K to 0.30 ± 0.02 at 1060 K, with the concomitant decrease of $\beta$ from 0.89 ± 0.04 to 0.70 ± 0.03. The two independent measurements indicate for the first time that the relationship $\alpha + \beta = 1$ holds quantitatively throughout the temperature range studied.

Introduction

The branching ratio of the products formed in the NH$_2$ + NO reaction, a process of great influence in the efficiency of NH$_3$ as a de-NO$_x$ agent, has been the subject of much controversy and discussion recently.1–7 The reaction is believed to take place primarily by the following two product channels:

\[
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2\text{H} + \text{OH} \quad (1)
\]

\[
\rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (2)
\]

The recent suggestion of a possible third channel at high temperatures by Stephens et al.5 could be accounted for by secondary radical reactions which do not produce either OH or H$_2$O.8

The branching ratio for OH production by reaction 1, $\alpha = k_i/(k_1 + k_2)$, reported by Atakan et al.5 as well as by Stephens and co-workers8 in the temperature range 298 ≤ T ≤ 1,200 K, $\alpha$ ≤ 0.2, has been shown to be significantly lower than the value determined by modeling the burning velocity data of NH$_3$–NO flames, $\alpha$ ≥ 0.5 above 1500 K.9,10 In fact, Vandooren and co-workers9 concluded that a value as high as 0.9 is required to account for their burning velocity measured near 2000 K.

More recently, Glarborg and co-workers7 arrived at a temperature-dependent expression, $\alpha = 2.2 \times 10^{-3} + 7.0 T$ for the range of 300 < T < 1,400 K, which is sufficient for the modeling of thermal de-NO$_x$ data provided that the lifetime of N$_2$H is long compared to the theoretically predicted value.

The branching ratio for OH production suggested by Glarborg et al.7 in the temperature range 300–1400 K deviates significantly from the upper limits set by both Atakan et al.5 and Stephens and co-workers.6 There is an urgent need to resolve this discrepancy. In addition, the extrapolated value with Glarborg’s expression, $\alpha = 0.36$ at 1500 K, is noticeably lower than that required ($\alpha$ ≥ 0.5) to model the burning velocity of the NH$_3$–NO flame studied by Vandooren and co-workers.9 The gap, however, could be accounted for by a sharp increase in $\alpha$ from 0.28 ± 0.02 at 1000 K to 0.51 ± 0.02 at 1200 K as concluded in our recent kinetic modeling of the experimentally measured NH$_3$ and NO removal rates by FTIR spectrometry and of the H$_2$O formation rate reported by Poole and Graven12 using a gravimetric method. The theoretical basis of the drastic increase in the branching ratio for the NH$_2$ + NO reaction between 1000 and 2000 K is yet to be elucidated.

In the present study, we employ a mass spectrometric method to determine directly the production of H$_2$O and CO$_2$ from the laser-initiated reaction NH$_3$ with NO in the presence of added CO, which is utilized as a monitor for the OH radical by means of the well-known OH + CO → CO$_2$ + H reaction.13 In this preliminary study, the experiment was carried out for the temperature range 302–1,060 K, in which the majority of experimental data has been reported.3–6

Experimental Section

Branching ratio measurements for the NH$_2$ + NO reaction were performed in the temperature range 302–1060 K using the high-pressure mass spectrometric sampling technique developed by Saalfeld and co-workers.14,15 The sampling technique had been extensively applied by Gutman, Slagle, and collaborators16–18 in conjunction with the excimer-laser generation of radical reactants. NH$_2$ radical was produced by photolysis of NH$_3$ at 193 nm. The concentration of the NH$_2$ radical generated from the photodissociation reaction was typically 1.5–5.0% depending on reaction temperature and photolysis laser energy, which varied from 30 to 40 mJ.

The reaction was studied with a quartz tubular Saalfeld reactor with an inner diameter of 10 mm and a heated length of 150 mm; the reactor has a conical sampling hole of 120 μm diameter, properly aligned with the detecting axis of a quadrupole mass spectrometer (Extrel Model C50). For the elevated temperature experiment, the reaction tube was heated with a nichrome ribbon which was insulated with ceramic wool. The reactor temperature could be varied from 300 to 1100 K. The reaction temperature was measured with a movable type K thermocouple, located near the center of the reaction tube with accuracy and uniformity of 2 K across the reaction zone.

The detection chamber was separated from the reaction chamber by a metal plate with a 1.0 mm orifice skimmer (Beam Dynamics Model 1) mounted at the center. The skimmer was located 3.0 mm from the sampling hole. The supersonic expansion chamber was pumped with an Edwards Diffstak Model 1160 diffusion pump with a pumping speed of 1300 L/s, providing a base pressure of 10$^{-7}$ Torr. The detection chamber was evacuated with a Leybold turbomolecular pump having a pumping speed of 1000 L/s, giving a base pressure of 10$^{-8}$ Torr.
The reaction tube housed in the expansion chamber was pumped with an Edwards rotary vacuum pump equipped with an oil trap to prevent the back diffusion of oil vapor. During experiment, the pressures in the expansion chamber and the detection chamber were kept at \((5 \times 10^{-5})\) and \((5 \times 10^{-6})\) Torr, respectively.

The positive ion signals of NH₃, CO₂, and H₂O were obtained by electron impact ionization at 70 eV followed by QMS mass selection. The time-resolved transient signal was averaged over 500 laser shots and recorded with a Nicolet 450 digital waveform acquisition system. The repetition rate was kept at 5 Hz, allowing enough time between pulses for the NH₃ signal level to return to its initial value.

All experiments were carried out under slow-flow conditions and with an excess amount of NO \([\text{NO}] \gg [\text{NH}_3]\) so as to minimize NH₃ radical recombinations and other secondary reactions in the mixture of NH₃, CO, NO, and He with total pressure of \(5 \rightarrow 10\) Torr (mainly He diluent) in the reactor. The mixing of the reactants and additional helium buffer gas was achieved in a coiled stainless steel bellow tube prior to their introduction into the reactor. The concentration of each individual molecule was obtained by the following formula:

\[
[R] = 9.66 \times 10^{16} \frac{P F_R}{T F_T} \text{ molecules/cm}^3
\]

where \(\%\) denotes the percentage of each molecule in its gas mixture, \(P\) is the total reaction pressure, \(T\) is the reaction temperature, \(F_R\) is the flow rate of each gas mixture, and \(F_T\) is the total flow rate of all gases. The flow rates were measured by using mass flowmeters (Brooks, Model 5850C) and the gas pressure was measured with an MKS Baratron manometer.

NH₃ (Aldrich), CO (Matheson), CO₂ (Aldrich), and H₂O (deionized water) were purified by standard trap-to-trap distillation. NO (Matheson) was purified by vacuum distillation through a silica gel trap maintained at 195 K to remove impurities such as NO₂. Silica gel was preheated and diffusion pumped for 12 h at 420 K to remove any condensed water. He (99.9995%) was used without further purification.

### Results and Discussion

The product channel branching ratios of the NH₂ + NO reaction were measured by mass selected detection of H₂O and CO₂, which was produced by the reaction of the OH product with added CO molecules. The branching ratios for the production of NH₃ + OH and N₂ + H₂O are defined by \(\alpha = k_1/(k_1 + k_2)\) and \(\beta = k_2/(k_1 + k_2)\), respectively.

To determine the \(\alpha\) and \(\beta\) values, we kept the total rate constant \(k = k_1 + k_2\) for the NH₂ + NO reaction fixed for each temperature and only the relative values of \(k_1\) and \(k_2\) were varied. The total rate constant has been measured by many groups;\(^\text{3-6,8}\) the value recommended by Baulch et al.\(^\text{13}\) agrees closely with our recent determination.\(^\text{8}\) The actual number densities of each product molecule were calculated by using carefully prepared calibration mixtures of H₂O, CO₂, and He.\(^\text{19}\) In view of the fact that even under pseudo-first-order conditions, one cannot exclude radical–radical recombination and other secondary reactions\(^\text{8}\) kinetic modeling was carried out with the SENKIN program\(^\text{20}\) using a set of reactions\(^\text{8,11}\) to simulate the kinetics of the NH₃ + NO reaction at each experimental temperature. A randomly selected set of data for all temperatures studied is summarized in Table 1 together with kinetically modeled concentrations and branching ratios.

The results of our kinetic modeling for CO₂ and H₂O yields aided by sensitivity analysis indicate that the products derive predominantly from reactions 1 and 2, respectively. The modeled results are not affected by the lifetime of the N₂H radical with or without including the reaction

\[
\text{N}_2\text{H} + \text{NO} \rightarrow \text{N}_2 + \text{HNO}
\]

which is assumed to occur with the same rate constant as its isoelectronic analogue, HCO + NO → CO + HNO.\(^\text{21}\) To test the possible N₂H lifetime effect, as suggested by Glazborg and co-workers\(^\text{2}\) in their recent modeling of a more complex system containing NH₃, NO, O₂, and H₂O, we increased as well as decreased the adopted literature value for the rate constant of the N₂H + M = N₂ + H + M reaction\(^\text{22}\) by 2 orders of magnitude. No effect on the calculated yields of CO₂ and H₂O was observed. In fact, a similar test performed in the simulation of NH₃ and NO removal rates in the thermal reaction of the two compounds near 1000 K resulted in undetectable changes in the calculated rates. In practice, one can effectively write reaction 1 as NH₃ + NO = H + N₂ + OH with no detrimental consequences, particularly in the temperature regime of interest to the NH₃ de-NO, process above 1000 K.

The kinetically modeled values of \(\alpha\) and \(\beta\) based on the absolute yields of CO₂ and H₂O, respectively, are summarized in Figure 1 for the 302–1060 K temperature range. Each data point given in the figure represents the average value of five to seven separate runs. The value of \(\alpha\) increases gradually from 0.11 ± 0.02 at 302 K to 0.30 ± 0.02 at 1060 K, whereas that of \(\beta\) decreases from 0.89 ± 0.04 at 302 K to 0.70 ± 0.03. These two independent sets of experimental data indicate that the relationship \(\alpha + \beta = 1\) holds accurately from room temperature to 1000 K without significant deviation, supporting our earlier conclusion\(^\text{8}\) that the mysterious “third channel” of the NH₂ + NO reaction at high temperatures\(^\text{6}\) does not exist.

In Figure 2, we summarize the values of \(\alpha\) determined by various groups,\(^\text{2-7,11}\) including the results of our kinetic modeling\(^\text{11}\) of experimentally measured NH₃ and NO removal rates as well as of the H₂O formation rates reported by Poole and Graven\(^\text{12}\) covering the temperature range 940–1200 K, as alluded to above.

As is evident from the figure, the present value of \(\alpha = 0.30\)

### TABLE 1: Typical Reaction Conditions and Product Yield at Selected Temperatures Studied

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>([\text{NH}_3]_0)</th>
<th>([\text{CO}]_0)</th>
<th>([\text{NO}]_0)</th>
<th>(\text{exp.} [\text{CO}_2]^b)</th>
<th>(\alpha)</th>
<th>(\beta)</th>
<th>(\text{exp.} [\text{H}_2\text{O}]^b)</th>
<th>(\beta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>302</td>
<td>6200</td>
<td>59.74</td>
<td>3.01</td>
<td>78.51</td>
<td>264.2</td>
<td>0.119</td>
<td>0.10</td>
<td>0.116</td>
</tr>
<tr>
<td>527</td>
<td>6720</td>
<td>69.38</td>
<td>2.52</td>
<td>89.94</td>
<td>263.9</td>
<td>0.106</td>
<td>0.14</td>
<td>0.104</td>
</tr>
<tr>
<td>695</td>
<td>6950</td>
<td>57.29</td>
<td>1.11</td>
<td>73.05</td>
<td>293.9</td>
<td>0.048</td>
<td>0.18</td>
<td>0.048</td>
</tr>
<tr>
<td>800</td>
<td>3900</td>
<td>82.01</td>
<td>2.30</td>
<td>205.7</td>
<td>169.1</td>
<td>0.201</td>
<td>0.20</td>
<td>0.202</td>
</tr>
<tr>
<td>930</td>
<td>4010</td>
<td>86.32</td>
<td>1.89</td>
<td>215.2</td>
<td>172.4</td>
<td>0.195</td>
<td>0.24</td>
<td>0.194</td>
</tr>
<tr>
<td>1004</td>
<td>4500</td>
<td>99.08</td>
<td>2.20</td>
<td>247.1</td>
<td>188.8</td>
<td>0.279</td>
<td>0.28</td>
<td>0.286</td>
</tr>
<tr>
<td>1060</td>
<td>4120</td>
<td>88.96</td>
<td>1.82</td>
<td>221.5</td>
<td>179.4</td>
<td>0.225</td>
<td>0.30</td>
<td>0.256</td>
</tr>
</tbody>
</table>

\(^b\) The units of total pressure and all concentrations are in mTorr. The signal amplitude was taken at \(t = 15\) ms for CO₂ and \(t = 10\) ms for H₂O in their concentration plateau regions.
Brown and Smith. 10

...the temperature range 302–1060 K with no evidence of a third product channel. Both branching ratios $\alpha$ and $\beta$ were shown to be insensitive to the lifetime of the $N_2H$ radical assumed in the modeling of $H_2O$ and $CO_2$ yields. These results and those deduced from our recent kinetic modeling of the $NH_3 + NO$ thermal reaction data suggest that the value increases sharply from 0.27 at 1060 K to 0.51 at 1200 K, merging closely with the value recently reported from $NH_3−NO$ flame studies, $\alpha \geq 0.5$ at $T \geq 1500$ K. The mechanistic basis of such a dramatic increase in product branching with temperature deserves a comprehensive theoretical investigation.

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References and Notes


19. Four different $H_2O$, $CO_2$ and He mixtures were used to calibrate the m/z 18 and 44 signals for individual runs. The Pyrex bulbs employed for these calibration mixtures were first saturated with several Torr of $H_2O$ and then evacuated for preparation of samples. The $H_2O$ concentrations obtained from the m/z 18 signals using various calibration mixtures agreed closely.


